

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS ✓
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**



(21) (A1) **2,253,119**
(22) 1998/11/09
(43) 1999/05/13

Rel. to corresp. to EP 916,647

(72) KÖNIG, Eberhard, DE

(72) SCHÜTZE, Detlef-Ingo, DE

(72) MEIXNER, Jürgen, DE

(71) BAYER AKTIENGESELLSCHAFT, DE

(51) Int.Cl.⁶ C08L 75/04, C07C 229/12, C08J 3/07, C09D 175/04

(30) 1997/11/13 (19750186.9) DE

(54) **PRECURSEUR D'AGENT D'HYDROPHILISATION, PROCEDE
PERMETTANT DE LE PREPARER ET DE L'UTILISER
COMME AGENT DE DISPERSION DU POLYURETHANE
AQUEUX**

(54) **HYDROPHILIZING AGENT PRECURSOR, A PROCESS FOR ITS
PREPARATION AND ITS USE AS A DISPERSING AGENT FOR
AQUEOUS POLYURETHANE DISPERSION**

(57) A new hydrophilizing agent precursor made by Michael addition of 1-amino-3,3,5- trimethyl-5-aminomethyl-cyclohexane with an .alpha.,.beta.-unsaturated carboxylic acid; its preparation and use, particularly as a dispersing agent in aqueous polyurethane dispersions.



**HYDROPHILIZING AGENT PRECURSOR, A PROCESS FOR ITS PREP-
ARATION AND ITS USE AS A DISPERSING AGENT FOR AQUEOUS
POLYURETHANE DISPERSION**

ABSTRACT OF THE DISCLOSURE

A new hydrophilizing agent precursor made by Michael addition of 1-amino-3,3,5-trimethyl-5-aminomethyl-cyclohexane with an α,β -unsaturated carboxylic acid; its preparation and use, particularly as a dispersing agent in aqueous polyurethane dispersions.

HYDROPHILIZING AGENT PRECURSOR, A PROCESS FOR ITS PREP-
ARATION AND ITS USE AS A DISPERSING AGENT FOR AQUEOUS
POLYURETHANE DISPERSION

5

FIELD OF THE INVENTION

The present invention relates to a new hydrophilizing agent and its preparation and use, in particular as a dispersing agent in aqueous polyurethane dispersions.

BACKGROUND OF THE INVENTION

10 It is known that NCO prepolymers are hydrophilized by reaction with suitable molecules with ionic groups, e.g., carboxylate anions. It is also known that polyurethanes hydrophilized in this way can be converted into polyurethane plastics which can then be dispersed in water for the production of coatings for substrates such as textiles, sheet metals, stone or wood. A review article by Rosthauser and
15 Nachtkamp in "Advances in Urethane Science and Technology", Volume 10, page 121-162 (1987) summarizes the knowledge in this field.

ACS Registry Number 84540-26-1 discloses β -Alanine, N-[(5-amino-1,3,3-trimethylcyclohexyl)methyl]-,monopotassium salt. British Patent 1,339,357, (British
20 version of DE-A 2,034,479), discloses dispersing agent building blocks made with the alkali metal salt of the addition product of an α -olefinic carboxylic acid, i.e., acrylic acid, and an aliphatic diprimary diamine. Alkali metal salts used to make the alkali metal salt of the addition product of an α -olefinic carboxylic acid and a diamine are prepared from the hydroxides, carbonates or bicarbonates of sodium,
25 potassium or lithium. The alkali metal salts are critical, and there is no suggestion that the polyurethane lattices can be made without the alkali metal salt of the addition product of an α -olefinic carboxylic acid and a diamine. There is no suggestion that cyclic diamines, e.g., isophorone diisocyanate, can be used. The agents can be used to make polyurethane lattices, which when dried, are intended to have little tendency
30 to swell in water and suitable resistance to water. To make the polyurethane lattices, a prepolymer containing isocyanate group reacts with the alkali metal salt of the

- 2 -

addition product of an α -olefinic carboxylic acid and an aliphatic diamine.

These agents are disadvantageous because they are permanently hydrophilized (due to the presence of the non-volatile base content, e.g., sodium), and do not have the lower hydrophilicity that is desired in some applications. Correspondingly, the coatings formed by the dispersing agents after being applied and stoving of a polyurethane dispersion such that the textile coatings or the lacquers produced with them still have an increased sensitivity to water. It would be desired to develop a hydrophilizing agent sufficiently versatile so that it can have either temporary hydrophilicity or permanent hydrophilicity. Another disadvantage of this group of dispersing agents is the intense yellow-brown intrinsic color, which manifests itself noticeably in a troublesome manner in pale-colored coatings.

The object of the invention is to overcome the disadvantages above, and therefore provide a dispersing agent which on the one hand is colorless and on the other hand can be temporarily hydrophilized or permanently hydrophilized. It is a further object of the invention to develop a simple process for making the dispersing agent. This object has been achieved with the discovery of the compound according to the invention.

SUMMARY OF THE INVENTION

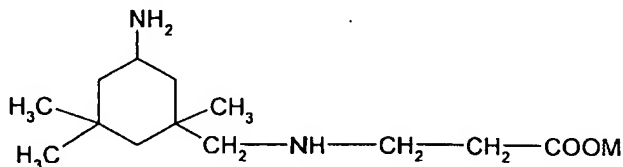
The invention relates to a hydrophilizing agent precursor prepared by the Michael addition of 1-amino-3,3,5-trimethyl-5-aminomethyl-cyclohexane with an α,β -unsaturated carboxylic acid. The term "Michael Addition" is known and refers to the overall addition to α,β -unsaturated carbonyl compounds in which an α,β -unsaturated carbonyl compound undergoes a nucleophilic attack at the end of the double bond further from the carbonyl group. The hydrophilizing agent precursor can be permanently or temporarily neutralized to form a hydrophilizing agent, depending on the desired application. The invention also relates to the use of the hydrophilizing agent as a chain lengthener of NCO prepolymers for use in the preparation of an aqueous polyurethane dispersion. The invention also relates to a hydrophilized polyurethane coating on a substrate, e.g., leather and textiles.

- 3 -

DETAILED DESCRIPTION OF THE INVENTION

The invention relates to a hydrophilizing agent precursor prepared by Michael addition of 1-amino-3,3,5-trimethyl-5-aminomethyl-cyclohexane with an α,β -unsaturated carboxylic acid. IPDA is a known compound which can be obtained from commercial sources. The α,β -unsaturated carboxylic acids include but are not limited to acrylic acid, methacrylic acid or crotonic acid and can also be obtained commercially. Generally, the α,β -unsaturated carboxylic acid is used in an amount ranging from 1 to 2 mol. Specific amounts are given in the examples below or can be readily obtained with routine experimentation. The fact that an α,β -unsaturated acid is reacted directly with IPDA and that this reaction product is a storage stable, almost colorless compound is essential to the invention. This storage-stable compound can be incorporated into NCO prepolymer chains and then neutralized.

Preferably, the invention relates to the Michael addition product of IPDA and acrylic acid, in which a compound mixture of unreacted IPDA, mono-adduct and di-adduct forms. The mono-adduct predominantly formed has the formula



in which

20

M represents H, an alkali/alkaline earth metal, such as Na, K, $^{1/2}\text{Ca}$ or $^{1/2}\text{Mg}$, or an amine moiety. Suitable amine moieties include NH_4^+ and $\text{N}(\text{R})_3$, where R is methyl, ethyl and/or hydroxyethyl.

25 The hydrophilizing agent precursor of the invention is neutralized permanently or temporarily, depending on the needs of a specific application. Suitable neutralizing agents for temporary hydrophilization include but are not limited to (i) volatile tertiary amines, e.g., dimethyl ethanol amine or triethylamine, and (ii) diprimary

- 4 -

amines which can be incorporated by isophoronediamine or 4,4' diamino-dicyclohexylmethane, and the like. Suitable neutralizing agents for permanently hydrophilization include metal bases, e.g., alkali/alkaline earth metal hydroxide. Generally, the neutralizing agent is used in an amount up to the equivalent of the COOH groups. Specific amounts of the neutralizing agent are given in the examples below or can be readily obtained with routine experimentation.

The hydrophilizing agent precursor according to the invention can be used in any way to meet the objects of the invention. The hydrophilizing agent precursors according to the invention, for instance, can be prepared by first introducing 1 mol of IPDA into a reaction vessel, preferably in water or isopropanol. α,β -unsaturated carboxylic acid, e.g., acrylic acid, can then be added dropwise into the reaction vessel at room temperature with stirring. The reaction manifests itself by a slight exothermicity. After the addition of the acid, the mixture is subsequently stirred at 40°C for 1 hour, and a clear colorless solution results. The clear and colorless solution of the hydrophilizing agent can then be suitably employed. For example, the solution can be added in a suitable amount to an acetonic NCO prepolymer solution at approx. 40°C, so that the hydrophilizing agent becomes incorporated into the polyurethane chains. Neutralization is then carried out with the calculated amount of base. It can then be decided whether a permanent hydrophilization, that is to say a neutralization with non-volatile metal hydroxides, or only a temporary hydrophilization, e.g., without an alkali metal. That is to say a neutralization with amines, is desired. An acetonic polyurethane solution can be dispersed in water in accordance with known techniques and further processed into an aqueous polyurethane dispersion for coatings by removal of the acetone by distillation. The preparation method generally does not utilize acyclic diamines. Specific amounts can be obtained by routine experimentation. Coatings can be made by applying the dispersion over a suitable substrate and drying the dispersion at a suitable temperature, e.g., 80°C.

The resulting film (coating) has properties which are suitable for substrates such as

- 5 -

textile materials, paper, plastics, metals, and glass. Film properties can be characterized by determining the film's modulus, tensile dry strength, elongation at break dry, tensile wet strength, elongation at break wet, and the like. Example 5 below shows film properties of a coating prepared in accordance to the invention.

5 Properties of other coatings can be determined by routine experimentation.

As already mentioned in part, the hydrophilizing agents according to the invention have the following advantageous properties:

- easy preparation
- 10 - no yellow coloration, and instead colorlessness
- possibility of choice of salt formation with non-volatile bases (metal hydroxides) or with volatile bases (amines)
- good compatibility with NCO prepolymers
- extension of the range of carboxylate-containing dispersing agents available.

15

The last two points are explained as follows. Carboxylate-containing hydrophilizing agents have a weaker permanent hydrophilicity than sulfonate-containing hydrophilizing agents, and for this reason the former are also preferred for aqueous lacquer applications or textile coatings with a high level of properties. However,

20 only few such hydrophilization building blocks exist on the market, such as carboxylate-containing compounds of dimethylolpropionic acid.

The hydrophilizing agents according to the invention supplement the range available in this respect and extend the possibilities of combinations of chemicals, because the

25 new hydrophilizing components are based on the IPDA hard segment, which is known to have a good compatibility. They are therefore particularly suitable for coating surfaces of the most diverse working substances and materials, e.g., textile materials, paper, plastics, metals, glass, etc., can be coated with them.

30 The invention is further described in the following illustrative examples. All parts are by weight unless otherwise indicated.

- 6 -

EXAMPLESExample 1Batch:

85.0 g	(1 eq NH ₂)*	isophoronediamine
36.0 g	(0.5 mol)	acrylic acid
282.0 g		water
<hr/>		
403.0 g	(1 eq NH/NH ₂)	dispersing agent solution
		solids: calc. 30%
		1 acid equivalent: 806 g

* based on the C=C double bond

Procedure:

5 IPDA and water were initially introduced into the reaction vessel at room temperature. Acrylic acid was added dropwise to this mixture, while stirring, the mixture warming slightly. When the addition of the acrylic acid has ended, the mixture was subsequently stirred at 45°C for 1 hour. A clear, colorless dispersing agent solution (30%) with an NH/NH₂ equivalent weight of 403 g and an acid equivalent of 806 g was obtained.

10

This dispersing agent solution can also easily be prepared in concentrated form, for example 50 or 60%. However, there was then the risk of crystallizing out at room temperature. Nevertheless, if these high-solids variants were stored at 60 to 70°C, they also remain liquid.

15

- 7 -

Example 2 (use example)Batch:

235.0 g	(0.236 eq)	of a polycarbonate based on hexane-1,6-diol of OH number 56
80.0 g	(0.080 eq)	of a polytetramethylene glycol of OH number 56
10.0 g	(0.020 eq)	of a monofunctional ethylene oxide polyether of molecular weight 500
4.3 g	(0.064 eq)	dimethylpropionic acid
33.6 g	(0.400 eq)	1,6-diisocyanatohexane (HDI)
35.6 g	(0.320 eq)	1-isocyanato-3,3,5-trimethyl-5-isocyanato-methyl-cyclohexane (IPDI)
28.2 g	(0.070 eq)	dispersing agent according to Example 1
7.65 g	(0.090 eq)	1-amino-3,3,5-trimethyl-5-aminomethyl-cyclohexane (IPDA)
8.08 g	(0.08 eq)	triethylamine
612.0 g		water
<hr/> 1,055.43 g		dispersion (40%)
		viscosity (23°C) approx. 900 mPa·s

5 Procedure:

The above polyols were dewatered at 100°C under 40 mbar for 30 min. and cooled to approx. 90°C. The two diisocyanates were added all at once, while stirring, and the reaction was carried out at 90°C for approx. 2 hours. An NCO content of 3.2% was measured, the calculated content being 3.36%. The mixture was diluted with 400 g acetone and a mixture of aqueous dispersing agent solution, IPDA and triethylamine was added to the acetonic NCO prepolymer solution, which has been heated to approx. 45°C. Thereafter, the mixture was subsequently stirred at 45°C for approx.

- 8 -

another 1 hour and dispersed with water. After the acetone has been distilled off (45°C/100 mbar), a milky-blue dispersion with a solids content of approx. 40% and a viscosity (23°C) of approx. 900 mPa·s was obtained.

- 5 As a leather coating, the dispersion has suitable fastnesses to creasing, in particular cold creasing (over 10,000 at -10°C and -30°C).

Example 3

- 10 This example describes the preparation of the hydrophilizing agent in an organic solvent.

Batch:

170.0 g	(2.0 eq)	isophoronediamine
72.0 g	(1.0 mol)	acrylic acid
358.0 g		isopropanol
<hr/>		
600.0 g	(2.0 eq NH/NH ₂)	dispersing agent solution
		solids: calc. approx. 40%
		1 acid equivalent: calc. 600 g

- 15 Procedure:

- Isophoronediamine and isopropanol were initially introduced into the reaction vessel and heated up to 40°C. Acrylic acid was added dropwise to this mixture, while stirring, a slight exothermicity being observed. After the addition of the acrylic acid,
- 20 the mixture was subsequently stirred at 45°C for 2 hours. A ready-to-use colorless dispersing agent solution with an NH/NH₂ equivalent of 300 g and an acid equivalent of 600 g was obtained

- 9 -

Example 4 (according to the invention)

In contrast to Example 1, there is a 10% neutralization of the carboxyl groups with KOH here.

5

Batch:

85.0 g	(1 eq NH ₂)	isophoronediamine
36.0 g	(0.5 mol)	acrylic acid
282.2g		water
2.8 g	(0.05 mol)	potassium hydroxide
406.0 g	(1.0 eq NH/NH ₂)	dispersing agent solution
		solids: calc. approx. 30.1%
		1 acid equivalent: 902 g

Procedure:

- 10 The procedure was as described in Example 1, and when the reaction has ended, the stated amount of solid potassium hydroxide was also stirred in. A clear, colorless dispersing agent solution (approx. 30%) which already contains permanent salt groups to the extent of 10 equivalent % and also 90 equivalent % non-neutralized carboxyl groups was obtained. The equivalent weight, based on the NH or NH₂
- 15 groups was 406 g.

Example 5 (use example)

- 20 In this example, neutralization of the dispersing agent was carried out to the extent of 30 equivalent % with 4,4'-diamino-dicyclohexyl-methane, which was incorporated during curing (heat) of the coating. Consequently, a permanent hydrophilization of only 10 equivalent % on the part of the KOH exists in the cured coating.

- 10 -

Batch:

49.5 g	(0.022 eq)	of a monofunctional ethylene oxide/propylene oxide polyether of OH number 25
80.0 g	(0.080 eq)	of a polypropylene glycol of OH number 56
110.0 g	(0.110 eq)	of a polycarbonate based on 1,6-dihydroxyhexane of OH number 56
110.0 g	(0.110 eq)	of a propylene oxide polyether started on trimethylolpropane of OH number 56
76.5 g	(0.612 g)	4,4'-diisocyanato-diphenylmethane
12.18 g	(0.14 eq)	butanone oxime
60.90 g	(0.15 eq)	dispersing agent according to Example 4
14.70 g	(0.14 eq)	4,4'-diamino-dicyclohexylmethane
533.57		water
<hr/> 1047.35 g		dispersion
		solids: 45%
		viscosity (23°C): approx. 500 mPa·s

Procedure:

- 5 The above polyols were dewatered at 100°C under 20 mbar and cooled to approx. 60°C. Thereafter, the total amount of polyurethane MDI was added all at once, while stirring, the mixture was heated slowly to 70°C and the reaction was carried out at this temperature for approx. 3 hours, until the NCO content has fallen to approx. 2.75%, an NCO content of 2.86% being calculated. The mixture was diluted with
- 10 500 g acetone and brought to approx. 40°C, and another control NCO measurement was carried out. An NCO content of approx. 1.2% was found, the calculated content being 1.3%. Thereafter, butanone oxime was added, the mixture was stirred at 40°C for approx. 20 min and an NCO content of approx. 0.58% was determined, the

- 11 -

calculated content being 0.67%. The dispersing agent solution according to Example 4 was then added and the mixture was subsequently stirred at 40°C for approx. 30 min, until no further NCO content was detectable. The diamine was now stirred in, and after approx. 15 min. the mixture was dispersed with water. After the acetone
5 has been distilled off (45°C/100 mbar), a milky-blue dispersion with a solids content of 45% and a viscosity at 23°C of approx. 500 mPa·s was obtained. In spite of the potentially reactive character, the dispersion was stable on storage.

Properties of the coating from the above dispersion

10 The dispersion was processed to a film or a gluing layer between PVC and polyamide according to a particular drying program (approx. 1 min. 80°C, approx. 1 min. 120°C and approx. 1 min. 140°C).

Film properties:

15	100% modulus	2.3 MPa
	Tensile strength dry	11.0 MPa
	Elongation at break dry	490%
	Tensile strength wet	8.8 MPa
	Elongation at break wet	510%
20	Swelling vol. EE	502%
	Swelling vol. H ₂ O	33%
	Film weight	70 g/m ²

Adhesive strength on polyamide:

25	dry	(N/2.5 cm)	34
	wet	(N/2.5 cm)	18

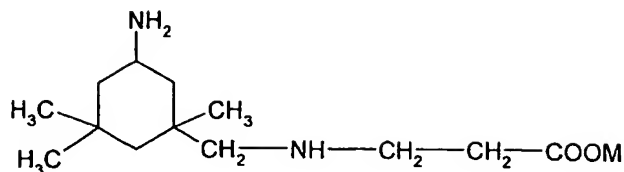
Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that
30 variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention.

- 12 -

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:-

1. A method for making an aqueous polyurethane dispersion comprising the sequential steps of:
 - 5 (a) reacting (i) 1-amino-3,3,5-trimethyl-5-amino-methyl-cyclohexane with (ii) an α,β -unsaturated carboxylic acid to form a hydrophilizing agent precursor; and
 - 10 (b) adding the hydrophilizing agent precursor to an NCO prepolymer solution,
 - (c) adding a neutralizing agent to the prepolymer solution in an amount up to the equivalent of the COOH groups to form the hydrophilizing agent, the neutralizing agent comprising a component selected from
15 the group consisting of alkali/alkaline earth metal hydroxides and amines.
 - (d) dispersing the polyurethane solution in water to form the polyurethane dispersion.
20
2. The method of Claim 1, wherein the α,β -unsaturated carboxylic acid is used in an amount ranging from about 1 to 2 moles.
- 25 3. The method of Claim 1, wherein the α,β -unsaturated carboxylic acid comprises a component selected from the group consisting of acrylic acid, methacrylic acid and crotonic acid.
- 30 4. The method of Claim 1, wherein the hydrophilizing agent comprises a component having the formula:

- 13 -



wherein

M consists of an alkaline metal and an amine moiety.

- 5 5. The method of Claim 1, wherein the method does not utilize acyclic diamines.
- 10 6. The method of Claim 1, wherein the method does not utilize an alkali metal as a neutralizing agent.
7. The hydrophilizing agent used to make the polyurethane dispersion of Claim 6.
- 15 8. The polyurethane dispersion formed by the method of Claim 1.
9. A coating formed by applying the polyurethane dispersion of Claim 8 on a substrate to form a liquid coating and drying the liquid coating.
- 20 10. The coating of Claim 9, wherein the substrate comprises a component selected from the group consisting of textile materials, paper, plastics, metals, and glass.
11. A method for making an aqueous polyurethane dispersion by
 - 25 (a) combining a hydrophilizing agent with an NCO prepolymer solution, and (b) dispersing the polyurethane dispersion in water;

- 14 -

wherein the hydrophilizing agent is made by:

- 5
- (i) reacting (i) 1-amino-3,3,5-trimethyl-5-amino-methyl-cyclohexane with (ii) an α,β -unsaturated carboxylic acid to form a hydrophilizing agent precursor; and
- 10
- (ii) adding a neutralizing agent to the precursor solution in an amount up to the equivalent of the COOH groups to form the hydrophilizing agent, the neutralizing agent comprising a component selected from the group consisting of alkali/alkaline earth metal hydroxides and amines.

12. The dispersion of Claim 11.